ELSEVIER

Journal of Organometallic Chemistry 566 (1998) 29–35

Journal of Organometallic Chemistry

Study of the planarization of the tricordinate phosphorus in phospholes; photoelectron spectra and structure of partially planarized phospholes

László Nyulászi [a,*], László Soós [a], György Keglevich [b]

[a] *Department of Inorganic Chemistry, Technical University of Budapest, H-1521 Budapest Gellért tér 4, Hungary*
[b] *Department of Organic Chemical Technology, Technical University of Budapest, H-1521 Budapest Müegyetem rakpart 3, Hungary*

Received 27 November 1997

Abstract

The gradual flattening of the tricoordinate phosphorus in phosphole by the increasing steric bulk of the substituent group is shown on the HF/6-31G* optimized geometries of alkylarylphospholes. By the decreasing pyramidality, aromaticity indices show increase, as a result of the increased conjugation. The aromaticity of 1-(2,4,6-tri-tertiarybutyl)-phosphole is similar to that of furan according to the geometrical indices. In the photoelectron spectra of the alkylaryl substituted phospholes the phosphorus lone pair ionization energy also decreases along the decreasing pyramidality. 1-(2,4,6-tri-Tertiarybutyl-phenyl)-3-methylphosphole has the lowest ionization energy value ever reported for a phosphole. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Phospholes; Aromaticity; Photoelectron spectra; Ab initio calculations

---

1. Introduction

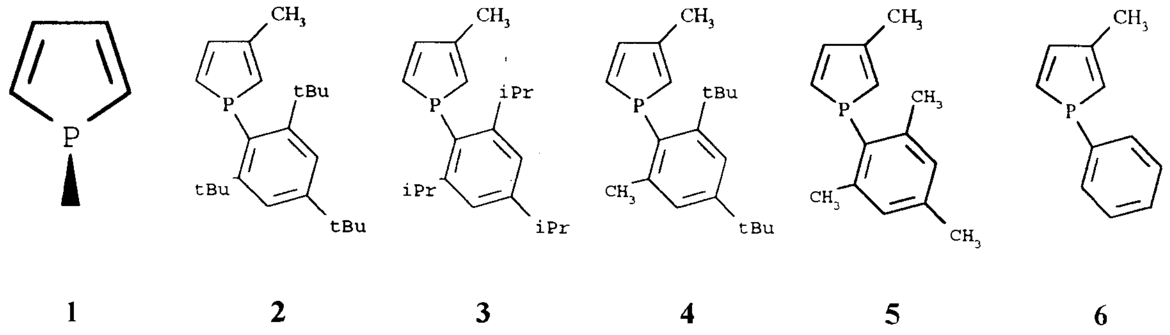
Phosphole (**1**) belongs to the simplest heterocyclic species. It is not aromatic in contrast to its congeners pyrrole and thiophene [1]. As it has been suggested by Mislow [2], the lone pair of the inherently nonplanar tricoordinate phosphorus [3] is unable to take part in the conjugative interaction with the π-system. Planar phosphole, however, which is not a minimum but a first order saddle point on the potential energy hypersurface, would be among the most aromatic five-membered heterocycles according to computational investigations [4–6]. Although not yet synthesized, pentaphosphole [6–8], and 1-(2,4,6-tri-tertiarybutyl)-1,2,4-triphosphole [9] are planar according to ab initio calculations. 1-(bis-trimethylsilyl-methyl)-3,5-bis-trimethylsilyl-1,2,4-triphosphole has recently been synthesized and characterized structurally as a planar compound [10]. All these planar systems are highly aromatic according to geometric and magnetic or energetic measures of aromaticity [6–11].

Planarization of phosphole itself, however, is only partially successful up to now. To achieve some flattening of the phosphorus pyramid Quin and Keglevich used bulky substituents on phosphorus [12–15]. The flattening—as measured conveniently by the bond angle sum about the tricoordinate phosphorus—in 1-(2,4,6-tri-tertiarybutyl)-3-methyl-phosphole (**2**) is 331.7° [12]. This value is considerably larger than in 1-benzyl-phosphole [16] (302.7°). According to Schmidpeter's classification [17], with a bond angle sum of 330–340° a significant planarization is achieved and the tricoordinate phosphorus can be considered as an intermediate state between phosphane and bis-methylene-phosphorane [18]. Schmidpeter achieved flattening of the phosphorus pyramid by using π-electron acceptor groups (PPh_3^+). Quantum chemical calculations also indicate some flattening of the tricoordinate phosphorus, when the phosphole ring is substituted by π-electron acceptor groups (e.g. BH_2) [5].

---

* Corresponding author.

PII S0022-328X(98)00685-8



Scheme 1.

Recent theoretical studies [6] have demonstrated that the reduction of the pyramidality of the tricoordinate phosphorus in phosphole is correlated with the increase of the aromatic character. The use of bulky substituents on phosphorus (as in **2**–**4**), results indeed in an enhancement of the aromatic character. 1-(2,4,6-tri-Tertiarybutyl)-3-methylphosphole (**2**) is the first phosphole showing electrophilic substitution reactivity [12]. Also the Bird aromaticity index (BI) [19] calculated from the X-ray structural data of **2** (56.5) [12] is clearly higher than for 1-benzyl-phosphole (35.5) [20]. Bond length equalization [6,11,17], and complex formation characteristic for aromatic compounds (the first η^5-complex of a phosphole [21]) is also observed for partially planarized 1,2,4-triphosphole (Scheme 1). The decrease of pyramidality of phosphorus, and the increasing aromaticity could be shown by a combined photoelectron spectroscopic quantum chemical investigation of the phosphorus lone pair ionization energy in case of 1-(di-tert-butyl-tolyl)-3-methyl-phosphole (**4**) [22]. In the present work our aim is to extend the previous investigations to a series of phospholes substituted on the phosphorus atom with aryl groups of different steric bulk. Photoelectron spectroscopy is used to study the interaction of the phosphorus lone pair with the π-system at differently pyramidalized phosphorus.

While **2** [12], **3** [15] and **4** [13,14] have been synthesized earlier, 1-mesityl-phosphole (**5**) has been prepared for the photoelectron spectroscopic investigations in the present study. Instead of the photoelectron spectrum of 3-methyl-1-phenyl phosphole (**6**) that of 1-phenyl-phosphole (**6′** published earlier [23]) will be discussed.

2. Results and discussion

To get initial structures for the ab initio calculations and to obtain a general overview about the effect of the substituents, first semiempirical calculations were carried out by the MNDO method. Since one important parameter from the point of view of the present study is the inversion barrier about phosphorus, first we calculated the MNDO and ab initio values to test the reliability of the method of our choice. For the inversion barrier about the tricoordinate phosphorus atom in phosphole 20.3 kcal mol^{-1} was calculated by using the MNDO method. At the HF/6-31G*, MP2/6-31G* and B3LYP/6-311 + G** levels, 26.4 [5], 17.19 [5] and 18.0 [6] kcal mol^{-1} were obtained, respectively. The inversion barrier of a substituted (1-isopropyl-2-methyl-5-phenyl)phosphole was 17 kcal mol^{-1} as determined by NMR spectroscopy [2]. The comparisons indicate that preliminary MNDO calculations will provide a reasonable estimate for the pyramidality problem of the tricoordinate phosphorus in phospholes. Results of further calculations on the out of plane (OOP) angle about phosphorus (see Fig. 1) with bulky P-substituents are summarized in Table 1.

The MNDO and the HF/6-31G* OOP angles are in reasonable agreement with each other, however, MNDO structures are somewhat more flattened (smaller OOPs) than those obtained by the ab initio calculation. The methyl substituent in the β position of the phosphole ring has only a small effect. Similarly, the *para* substituent on the phenyl ring also has a negligible influence on the OOP, in accordance with the expectations. Therefore—to save computer time—ab initio geometry optimizations of **2**, **3**, **4** and **5** were carried out only for model compounds (**2′**, **3′**, **4′** and **5′**, respectively), lacking the *para* substituent in the benzene ring, and the 3-methyl group on the phosphole ring. The OOP angles obtained are also in reasonably good agreement with the available X-ray structural data (see below).

The HF/6-31G* optimized structure of **2′** is shown in Fig. 2. All the other structures (**3′**–**5′**), are similar, with the phosphole and the phenyl rings being perpendicular to each other. Selected structural parameters of the

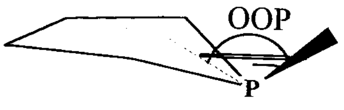
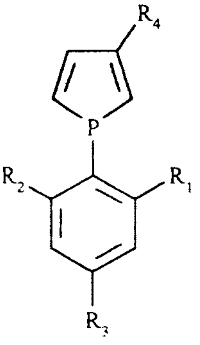


Fig. 1. Graphical definition of the OOP angle in phosphole.

Table 1
Effects of substituents (as shown in the drawing) on the OOP angle (in degree) on phosphorus, as calculated by the MNDO and ab initio methods



R_1	R_2	R_3	R_4		MNDO	HF/6-31G*	B3LYP/6-31G*	Exp.
—	—	—	—	1	73.6	74.3	73.6	
H	H	H	H	6′	62.0	68.3	67.1	
Me	Me	Me	H	5′	55.5	59.5		
Me	Me	Me	Me	5	55.5	59.4		
t-Bu	Me	Me	H	4′[a]	53.7	57.6	55.7	
Me	t-Bu	tBu	H		54.0			
Me	t-Bu	tBu	Me	4	54.1			
i-Pr	i-Pr	H	H	3′	52.6	58.0	56.4	
i-Pr	i-Pr	i-Pr	H		52.2			
i-Pr	i-Pr	i-Pr	Me	3	52.7			58.0[b]
t-Bu	t-Bu	H	H	2′	49.1	49.0		45.9[c]

[a] With Me group instead of H at the *p*-position of the phenyl ring.
[b] X-ray structure of 3 from [15].
[c] X-ray structure of 2 from [12].

HF/6-31G* optimized phospholes **2′**–**5′** are collected in Table 2. In accordance with the expectations, the bond angle sum at the tricoordinate phosphorus atom is increasing with the steric bulk of the substituent, as shown by the bond angle sum (SUMBA). Simultaneously, the C_2–P–C_5 angle in the ring is opening up. (For a planar tricoordinate phosphorus with sp^2 hybrid 120° bond angle would be expected. For the nonplanar tricoordinate phosphorus the bonding angles are somewhat larger than 90°.) With the increasing bulk of the substituent at phosphorus the PC bond shows shortening and the CC bond lengths approach each other in agreement with the expected increase of the conjugation in the ring. BI [19], and bond shortening index (BDSHRT) [25]—as shown in Table 2—are increasing simultaneously with the increasing steric bulk of the substituent. The geometrical parameters of phospholes **2′** and **3′** are in reasonably good agreement with the published X-ray structures, although for **2′** both the OOP angle (Table 1) and the SUMBA (Table 2) are somewhat underestimated at the HF/6-31G* level. The BI calculated from the experimental data was also somewhat larger than that obtained from the HF/6-31G* geometry [26]. To make a fair comparison, the BI and the BDSHRT of furan, thiophene and pyrrole, all calculated using data at the HF/6-31G* level [26], are also given in Table 2. According to the geometric aromaticity indices, **2′** has a similar aromaticity to

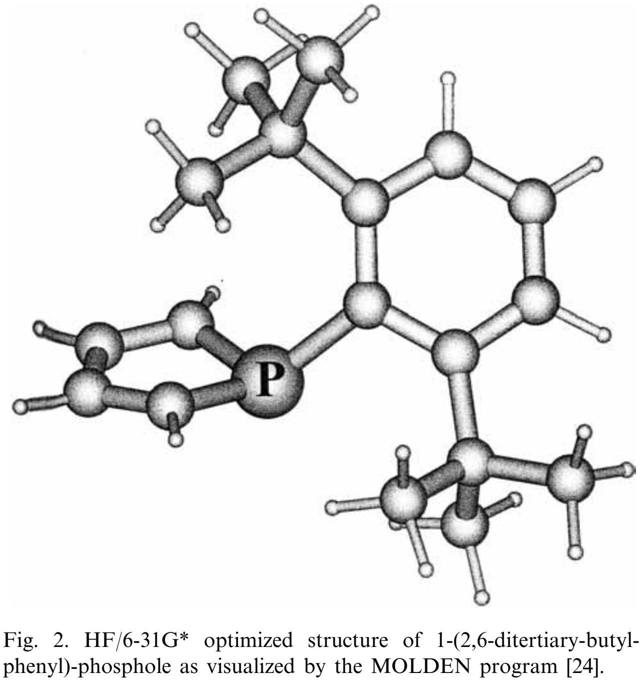
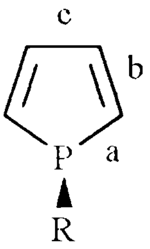


Fig. 2. HF/6-31G* optimized structure of 1-(2,6-ditertiary-butylphenyl)-phosphole as visualized by the MOLDEN program [24].

Table 2
Selected HF/6-31G* structural parameters and calculated geometrical aromaticity indices of phospholes 1-6 (in angstrom and degrees).



	a	b	c	CPC	SUMBA	BI	BDSHRT
1	1.821	1.332	1.471	89.7	291.3	33	49
6′	1.817	1.333	1.473	89.6	300.1	34	49
5′	1.807	1.337	1.466	90.3	312.3	40	50
4′	1.802	1.339	1.463	90.6	314.9	42	50
3′	1.803	1.340	1.464	90.5	314.3[a]	42	50
2′	1.790	1.342	1.459	91.3	325.5[b]	46	51
furan	1.362	1.361	1.431	106.6	—	46	49
thiophene	1.725	1.345	1.437	91.3	—	58	56
pyrrole	1.362	1.358	1.427	109.5	360.0	67	55

[a] From the X-ray structure of 3 [15] 314.4° was obtained as bond angle sum.

[b] From the X-ray structure of 2 [12] 331.7° was obtained as bond angle sum.

furan. It has been shown before [22] that the phosphorus lone pair has considerable participation in the π-system at OOP angles between 40 and 50°. Since phosphorus (due to its lower electronegativity) is a much better electron pair donor than oxygen, it takes part in the conjugation effectively, even if the overlap is unfavorable as a result of the nonplanarity.

The bulky substituent on the tricoordinate phosphorus atom decreases the inversion barrier significantly, in accordance with the expectations. For **2′** with the phosphorus atom under planarity constraint (but allowing all other parameters to relax) an inversion barrier of 10.98 kcal mol^{-1} was calculated at the HF/6-31G* level, that is smaller than that of **1** (26.5 kcal mol^{-1} at the same level [5]). For 1-(2,6,ditertbutylphenyl)phospholane the inversion barrier was 27.46 kcal mol^{-1}, that is clearly larger than for **2′**, but smaller than that for 1-methyl-phospholane (48.0 kcal mol^{-1}). Thus, the steric effect of the bulkiest substituent considered here is to reduce the inversion barrier by 15–18 kcal mol^{-1}.

The photoelectron spectra of the compounds under investigation (**2**–**5**) can be seen in Fig. 3, while the spectral data are collected in Table 3. The spectra are characterized by a band at low ionization energies and a broad bump. The distinct band has a shoulder at the low energy side for compounds **2**–**5**. According to the HF/6-31G* orbital energies, four ionizations should be expected in the region of low ionization energies (Table 3). Two of them are to be attributed to the π-ionizations of the substituting aryl ring. One ionization belongs to the unperturbed butadienic HOMO, and the fourth one to the phosphorus lone pair orbital. The two rings in **2′**–**5′** are perpendicular to each other according to the calculations (cf. Fig. 2). The same structure was suggested by crystallographic investigations [12,15] and

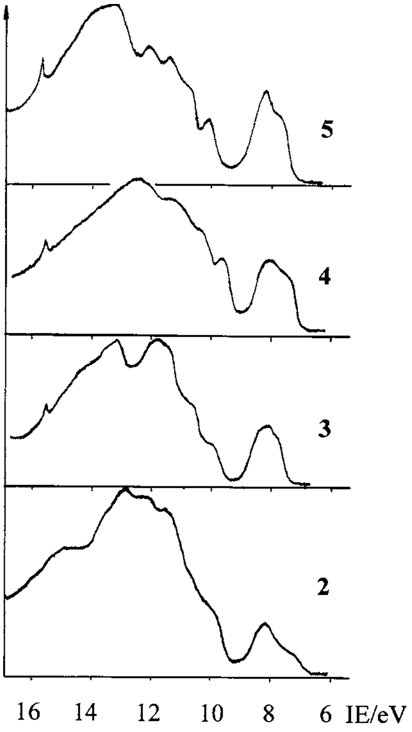


Fig. 3. Photoelectron spectra (intensities in cps) of the alkylaryl substituted phospholes **2**–**5**.

Table 3
HF/6-31G* (Koopmans) and measured ionisation energies of phospholes **2′**–**6′**[a] and **2**–**5** and **6′**, respectively, in eV

	6′ meas.	**6′** calc.	**5** meas.	**5′** calc.[a]	**4** meas.	**4′** calc.[a]	**3** meas.	**3′** calc.[a]	**2** meas.	**2′** calc.[a]
n_P	8.45	9.04	*8.1*[a]	8.89	*7.9*[a]	8.38	*7.9*[a]	8.52	*7.5*[a]	8.09
π_{CCCC}	8.45	8.50	8.58	8.41	8.35	8.40	8.21	8.54	8.34	8.47
π_{Ar}	9.25	9.14	8.58 (*8.42*)[b]	8.59	8.35 (*8.35*)[b]	8.62	8.21 (*8.26*)[b]	8.61	8.34 (*8.21*)[b]	8.70
		9.38		8.64		8.72		9.17		9.03

[a] The figures in italics indicate shoulders.

[b] The data in brackets are the measured π_{Ar} ionization energies of the aromatic moiety RH, corresponding to the alkylaryl substituent (R) on phosphorus. The ionization energies measured for mesitylene and 1,3,5-tri-tert-butylbenzene are in good agreement with those published in [27].

by the ^{13}C-NMR studies [14] earlier. Thus, no interaction can be expected between the phosphorus lone pair and the π-system of the aryl ring in **2**–**5**. Indeed, the maximum of the bands appears at the ionization energies, close to those measured for RH, where R is the substituting alkylaryl group on the phosphorus atom (see data in brackets in Table 3). For **2′**, **3′** and **4′** the HOMO is the phosphorus lone pair orbital, while for **5** and **6** it is the butadienic π-MO. Nevertheless, from the spectrum published [23] it was clear even for **6**, that the butadienic π and the phosphorus lone pair ionization energies contribute to one broad band, thus their energy difference is small. The shoulder at low ionization energies of phospholes **2**–**5** shows increasing separation from the lowest ionization energy band as the steric bulk of the substituent (and thus the OOP angle) increases. The phosphorus lone pair orbital is getting also destabilized—alongside with the flattening of the phosphorus pyramid—according to the calculations. This is in agreement with our earlier results [22], where methylphospholes were calculated with constrained OOP angle about the phosphorus atom. Also, between the first ionization energies of **2–5** and the calculated SUMBA of **2′**–**5′**, a linear correlation (cc. 0.959) was found. In accordance with the flattening of the phosphorus pyramid the lowest ionization energy (7.5 eV) is exhibited by the supermesityl-phosphole **2**. This 7.5 eV ionization energy of **2** is the lowest value ever reported for a phosphole. The decrease of the ionization energy is due to the increase of the p character of the lone pair orbital of phosphorus, which allows better overlap with the π-system, than in the case of **6** having a rather pyramidal phosphorus atom (see data for **6′** in Table 1) and consequently a large s character.

3. Conclusions

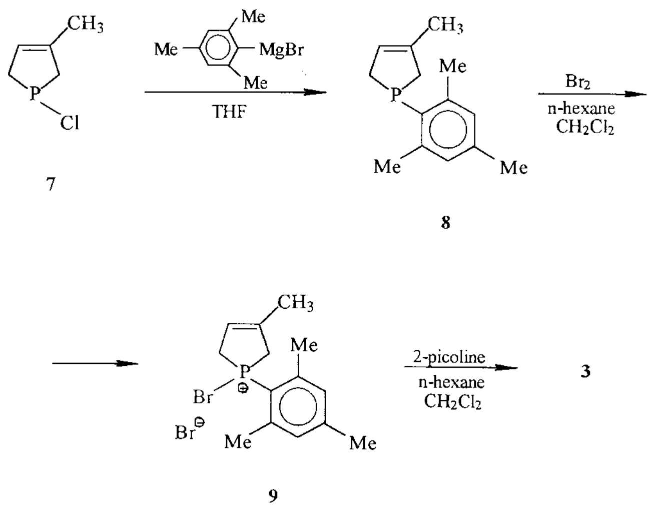
With the gradual flattening of the phosphorus pyramid due to the increasing space requirement of the P-substituent, the phosphorus lone pair ionization energy decreases in the phospholes investigated. 1-(2,4,6-tri-tertbutylphenyl)-3-Methylphosphole (**2**) has the lowest ionization energy value ever reported for a phosphole. The decrease of the ionization energy is in accordance with the increase in the p character of the corresponding orbital, as concluded from the calculated MOs. This allows for a better overlap with the butadienic π-system, resulting in bigger aromaticity with the increasing bulk of the substituent, as shown by the different geometric aromaticity indices, as the BI [19], or the BDSHRT [24]. Also the inversion barrier at the tricoordinate phosphorus decreases with the increasing steric bulk of the P-substituent.

Considering the twisting of the phenyl ring from the symmetrical position in **2′** [26], it seems apparent that additional increase of the steric bulk of a two dimensional phosphorus substituent results in only moderate further flattening of the phosphorus pyramid. Moreover, any attempted synthesis would be rather difficult due to the steric hindrance. Thus, the increase of the bond angle sum above 340° can only be conceived, when applying other substituents (e.g. π-electron acceptors, such as trimethylsilyl, or boryl which were shown to have effective before computationally [5]) on the carbon atoms of the phosphole ring.

4. Experimental section

Photoelectron spectra have been recorded at the He I resonance line on an instrument described earlier [27]. The resolution during the measurement was 40 meV at the $^2P_{1/2}$ Ar line. Quantum chemical calculations were carried out by using the Gaussian 94 package [28]. Preliminary calculations were carried out by the semiempirical MNDO method [29]. As a result of these calculations, model compounds (see below) were selected to account for the steric bulk of the substituents with a possibly minimum cost of computer time. Geometries of model compounds were fully optimized at the HF/6-31G* level.

The NMR spectra were taken on a Bruker DRX 500 spectrometer. The couplings are given in Hz. Mass spectra were recorded on a MS 25 RFA instrument at 75 eV. Aryl-phospholes **2**, **3** and **4** were prepared, as described earlier [12–15].



Scheme 2.

4.1. 3-Methyl-1-(2,4,6-trimethylphenyl)phosphole (5)

The solution of 2,4,6-trimethylphenylmagnesium bromide prepared from 18.3 g (0.093 mol) of 1-bromo-2,4,6-trimethylbenzene and 2.2 g (0.092 gatom) of magnesium in 70 ml of dry THF was added dropwise to the solution of 11.0 g (0.082 mol) of chlorophospholene **7** [30] in 70 ml of THF with stirring, at 0°C, in nitrogen atmosphere. After complete addition, contents of the flask were stirred at room temperature for 1 h. The solvent was removed by distillation in vacuum and the residue so obtained extracted with 4 × 100 ml of *n*-hexane to give 17.7 g (99%) of phospholene **8** after evaporating the solvent. MS, *m*/*z* (rel. int.) 218 (M^+, 100), 203 (26), 190 (12), 175 (15), 150 (22), 135 (34), 119 (10).

To 17.7 g (ca. 0.082 mol) **8** from the previous reaction dissolved in 400 ml of *n*-hexane was added the 25 ml dichloromethane solution of 4.2 ml (0.082 mol) of bromine with stirring at 0°C, over a period of 20 min. After addition was complete, the mixture was stirred at room temperature for 2 h. Phospholium bromide **9** appeared as a yellow precipitated material.

The *n*-hexane solution of **9** obtained in the previous reaction was treated with 16.2 ml (0.164 mol) of 2-picoline dissolved in 50 ml of dichloromethane. After stirring at room temperature for 20 h and at the boiling point for 24 h, the mixture consisted of two phases. The upper layer was decanted and concentrated in vacuum. The crude product so obtained was purified by column chromatography (silica gel, 3% methanol in chloroform) to give 8.2 g (44%) of phosphole **2** in a purity of 95%. ^{31}P-NMR ($CDCl_3$) δ -0.81; ^{13}C-NMR ($CDCl_3$) δ 18.9 ($J = 3.9$, C_3,–CH_3), 21.0 (C_4,–CH_3), 21.4 ($J = 15.5$, C_2,–CH_3), 125.7 ($J = 2.1$, C_2), 128.9 ($J = 5.4$, $C_{3'}$), 129.0 ($J = 13.8$, $C_{1'}$), 133.1 (C_5), 137.5 ($J = 13.0$, C_4), 140.1 (C_4), 144.6 ($J = 15.6$, C_3), 146.0 ($J = 15.6$, $C_{2'}$); ^{1}H-NMR ($CDCl_3$) δ 2.20 (d, $J \sim 1$, C_3–CH_3), 2.21 (s, C_2,–CH_3), 2.25 (s, C_4,–CH_3) total int. 12H, 6.42 (d, $J = 38.9$, 1H, C_2–H), 6.83–6.91 (m, 2H, C_4–H, C_5–H); MS *m*/*z*, (rel. int.) 216 (M^+, 100), 201 (27), 161 (26), 119 (16) (Scheme 2).

Acknowledgements

Financial support from OTKA Grants No T014955 and T014917 is gratefully acknowledged. We are grateful to K. Ujszászy and T. Kárpáti for the recording of the mass spectra and some of the photoelectron spectra, respectively. We also thank for Professor L.D. Quin for his continuous interest and advice.

References

[1] For comprehensive works see: F. Mathey, Chem. Rev. 88 (1988) 437; A.N. Hughes, in: R. Engel (Ed.), Handbook of Organophosphorus Chemistry, Marcel Dekker, New York, 1992, Chapter 10; L.D. Quin, in: A. Katritzky, C. Rees, W.E.F.V. Scriven (Eds.), Comprehensive Heterocyclic Chemistry, Vol. 2, Pergamon, Oxford, England, 1996, Vol. 2, pp. 757–856.

Aromaticity indices of different type are much smaller for phosphole than for other five membered rings;

K.K. Baldridge, M.S. Gordon, J. Am. Chem. Soc. 110 (1988) 4204; L. Nyulászi, T. Veszprémi, J. Réffy, B. Burkhardt, M. Regitz, J. Am. Chem. Soc. 114 (1992) 9080; V.I. Minkin, M.N. Glukhotsev, B.Ya. Simkin, Aromaticity and Antiaromaticity—Electronic and Structural Aspects, Wiley, New York, 1994; P.v.R. Schleyer, P.K. Freeman, H. Jiao, B. Goldfuss, Angew. Chem. Int. Ed. Engl. 34 (1995) 337.

[2] J.D. Andose, A. Rauk, K. Mislow, J. Am. Chem. Soc. 96 (1974) 6904.

[3] R.E. Weston Jr., J. Am. Chem. Soc. 76 (1954) 2645.

[4] D.B. Chesnut, L.D. Quin, J. Am. Chem. Soc. 116 (1994) 5779.

[5] L. Nyulászi, J. Phys. Chem. 99 (1995) 586.

[6] A. Dransfeld, L. Nyulászi, P.v.R. Schleyer, Inorg. Chem., in press.

[7] L. Nyulászi, Inorg. Chem. 35 (1996) 4690.

[8] M.N. Glukhotsev, A. Dransfeld, P. v, R. Schleyer, J. Phys. Chem. 100 (1996) 13447.

[9] L. Nyulászi, J.F. Nixon, J. Organimet. Chem., in press.

[10] F.G.N. Clokes, P.B. Hitchcock, P. Hunnable, J.F. Nixon, L. Nyulászi, E. Niecke, V. Thelen, Angew. Chem. Int. Ed. Engl. 37 (1998) 1083.

[11] L. Nyulászi, J. Phys. Chem. 100 (1996) 6194.

[12] Gy. Keglevich, Zs. Böcskei, Gy. Keserü, K. Ujszászi, L.D. Quin, J. Am. Chem. Soc. 119 (1997) 5095.

[13] L.D. Quin, A.S. Ionkin, R. Kalgutkar, Gy. Keglevich, Phosphorus Sulfur 109–110 (1996) 433.

[14] L.D. Quin, Gy. Keglevich, A.S. Ionkin, R. Kalgutkar, G. Szalontai, J. Org. Chem. 61 (1996) 7801.

[15] Gy. Keglevich, L.D. Quin, Zs. Böcskei, Gy.M. Keserû, R. Kalgutkar, P.M. Lahti, J. Organomet. Chem. 532 (1997) 109.

[16] P. Coggon, J.F. Engel, A.T. McPhail, L.D. Quin, J. Am. Chem. Soc. 92 (1970) 5779.

[17] G. Jochem, H. Nöth, A. Schmidpeter, Chem. Ber. 129 (1996) 1083.

[18] A. Schmidpeter, M. Thiele, Angew. Chem. 103 (1991) 333.

[19] C.W. Bird, Tetrahedron 41 (1985) 1409.

[20] C.W. Bird, Tetrahedron 46 (1990) 5697.

[21] V. Caliman, P.B. Hitchcock, J.F. Nixon, L. Nyulászi, L.N. Sakarya, J. Chem. Soc. Chem. Commun. (1997) 1305.

[22] L. Nyulászi, Gy. Keglevich, L.D. Quin, J. Org. Chem. 61 (1996) 7808.

[23] W. Schäfer, A. Schweig, G. Märkl, H. Hauptmann, F. Mathey, Angew. Chem. 85 (1973) 140.

[24] G. Schaftenaar, MOLDEN 2.5; Caos/CAMM Center Nijmegen, The Netherlands, 1994.

[25] L. Nyulászi, P. Várnai, T. Veszprémi, THEOCHEM. 358 (1995) 55.

[26] It is known that conjugative/aromatic stabilization effects are somewhat underestimated at the HF (while are overestimated at the MP2) level (see e.g. ref. [9]).This results in a reduction of aromaticity indices, when calculated from data obtained at the HF level. The underestimation of the aromatic stabilization at the HF level becomes apparent at larger OOP angles. Lacking (a part of) such a stabilization by using the HF procedure the optimized geometry is less planar than for the real structure. Also in case of **6**′ the phenyl ring is somewhat distorted from the symmetry plane of the phosphole ring, while in the X-ray structure of **6** this distortion is negligibly small. The distorted phenyl ring has a smaller steric repulsion than the symmetric one.

[27] J.O. Holwell, J.M. Gonclaves, C. Amatore, L. Klasinc, R.M. Wightman, J.K. Kochi, J. Am. Chem. Soc. 106 (1984) 3968.

[28] T.Veszprémi Gy. Zsombok, Magy. Kém. Foly. 92 (1986) 39.

[29] Gaussian 94, Revision B.2, M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.

[30] M.J.S. Dewar, W. Thiel, J. Am. Chem. Soc. 99 (1977) 4907.